



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
01.10.2003 Bulletin 2003/40

(51) Int Cl.7: **B22D 11/01**

(21) Application number: **03006039.6**

(22) Date of filing: **19.03.2003**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR
 Designated Extension States:
AL LT LV MK RO

(71) Applicant: **Howmet Research Corporation**
Whitehall, Michigan 49461 (US)

(72) Inventor: **McRae, Michael M.**
Spring Lake, Michigan 49456 (US)

(30) Priority: **29.03.2002 US 109043**

(74) Representative: **Hoeger, Stellrecht & Partner**
Uhlandstrasse 14 c
70182 Stuttgart (DE)

(54) **Method of making amorphous metallic sheet**

(57) A method of making a sheet (S) of amorphous metallic material (M) wherein molten metallic material capable of rapidly solidifying to an amorphous microstructure is discharged onto a flat, quiescent surface (20a) of a liquid cooling pool (20). The liquid cooling pool comprises a thermally conductive liquid material, such

as a molten metal or alloy, having a lower temperature than that of the amorphous metallic material discharged thereon. The molten metallic material is discharged onto the pool and assumes the width dimension of the pool. The solidified amorphous sheet is continuously removed from the pool surface at a location remote from where the molten material is discharged onto the pool.

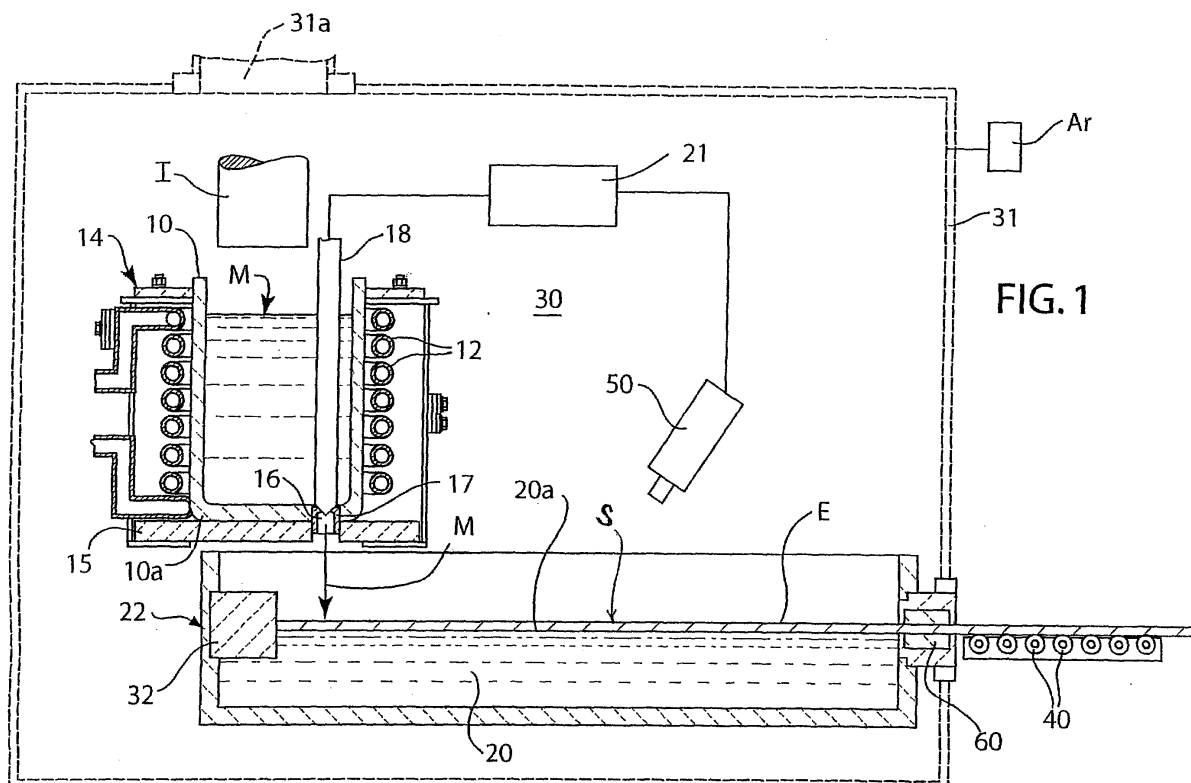


FIG. 1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method of making a thin sheet of amorphous metallic material.

BACKGROUND OF THE INVENTION

[0002] Amorphous (oftentimes called glassy) metallic materials have been made by rapid solidification processes. For example, amorphous metallic powder has been made by various types of atomization processes where the molten metallic material is discharged from an atomization nozzle, pressure and/or gas atomized, and rapidly cooled to solidify as amorphous powder particles. Amorphous metallic ribbon has been made by the so-called melt spinning process where the molten metallic material is discharged onto a rotating, cooled wheel to rapidly solidify as a flat ribbon. The width dimension of melt spun, flat ribbon has been limited by the relatively narrow width of the cooled wheel on which it is rapidly solidified. For example, melt spun ribbons typically have a width dimension not exceeding approximately 1 1/2 inches.

SUMMARY OF THE INVENTION

[0003] An embodiment of the present invention provides a method of making a sheet of amorphous metallic material wherein molten metallic material capable of rapidly solidifying to an amorphous microstructure is discharged onto a surface of a liquid cooling pool. The liquid cooling pool comprises a thermally conductive liquid material, such as a molten metal or alloy, having a lower temperature than that of the molten metallic material discharged thereon. The molten metallic material is discharged onto the pool and assumes a width dimension of the pool. This width dimension is imparted to the solidified amorphous sheet as the molten metallic material rapidly solidifies on the surface of the pool. The solidified amorphous sheet is removed from the pool surface at a location remote from where the molten material is discharged onto the pool. Molten amorphous metallic material is fed onto the pool surface at a rate to control the thickness dimension of the amorphous sheet.

[0004] The above and other advantages of the present invention will become more readily apparent from the following drawings taken in conjunction with the following detailed description.

DESCRIPTION OF THE DRAWINGS

[0005]

Figure 1 is a longitudinal sectional view of apparatus for practicing a method embodiment pursuant the invention.

Figure 2 is a plan view of the apparatus.

Figure 2 is a plan view of apparatus for practicing another method embodiment pursuant the invention.

Figure 4 is a longitudinal sectional view of apparatus for practicing still another method embodiment pursuant the invention.

DESCRIPTION OF THE INVENTION

[0006] The present invention provides a method of making a sheet S of amorphous metallic material wherein the sheet is considered to be amorphous when its microstructure is at least 50% amorphous or glassy, preferably when its microstructure is substantially 100% amorphous or glassy. The amorphous or glassy microstructure is a non-crystalline, non-ordered structure that is evident from X-ray diffraction patterns thereof.

[0007] Amorphous metallic materials which can be made into amorphous sheet by practice of the invention include, but are not limited to, aluminum based alloys, iron based alloys, titanium based alloys, zirconium based alloys such as Vitreloy amorphous alloy, and other amorphous alloys. When rapidly solidified at appropriate relatively high cooling rates, these metallic materials can produce an amorphous microstructure described above. Cooling rates on the order of 10^3 degrees F/second maximum may be involved. The invention can be practiced to make a sheet S of amorphous metallic material where a sheet for purposes of illustration and not limitation may have a width dimension of about 3 inches and above, such as for example about 4 to about 12 inches, and a thickness up to about 2 inches, such as for example about 0.1 inch to about 0.5 inch and above, with any desired length, the particular sheet dimensions achievable being dependent on the particular amorphous alloy being solidified.

[0008] Referring to Figure 1, molten metallic material M capable of rapidly solidifying to an amorphous microstructure is melted and heated to a selected casting temperature in an induction melting crucible 10 received within an induction coil 12 of a melting vessel 14. The crucible includes a rectangular shaped nozzle opening 16 in the bottom crucible wall 10a and in an underlying crucible support plate 15. The nozzle opening 16 is formed by a ceramic nozzle insert 17 received and sealed in crucible bottom wall 10a and crucible support plate 15. A complementary shaped ceramic nozzle stopper rod 18 is received in the nozzle opening 16 and is moved by stopper rod actuator 21 to close off and open the nozzle opening 16 in a manner to meter the molten metallic material onto a horizontal, quiescent upper surface 20a of liquid cooling pool 20 residing in a vessel 22.

[0009] Solid ingots I of the amorphous metallic material can be fed through a door 31a in housing 31 into the crucible 10 in a manner to provide continuous melting and supply of the molten metallic material onto the upper surface 20a of the pool 20. Alternately, pre-melted me-

tallic material can be supplied to the crucible 10 from a suitable source, such as a supply ladle and the like.

[0010] The crucible 10 and pool 20 can reside in a common chamber 30 of a housing 31 with the chamber 30 pressurized to a slight superambient pressure (e.g. greater than 1.1 atmospheres) using a source Ar of inert gas, such as argon, or other gas that is non-reactive with the molten metallic material M. The use of an inert or non-reactive gas atmosphere in chamber 30 controls (reduces) oxygen content of the chamber to avoid unwanted reaction of the molten and solidified amorphous metallic material with oxygen as well as other gases.

[0011] Alternately, as shown in Figure 4 where like features bear like reference numerals, the crucible 10 can reside in a melting chamber 33 disposed above the pool 20 and slightly pressurized with an inert or non-reactive gas atmosphere, while the pool 20 in vessel 22 is disposed in ambient air. The melting chamber 33 is pressurized slightly above atmospheric pressure using an inert or non-reactive gas and includes an opening 33a through which the molten metallic material can be discharged on to pool surface 20a. A blanket B of argon or other inert or non-reactive gas is provided by piping the argon gas (which is heavier than air) to reside above the top surface of the molten and solidified amorphous metallic material on the pool surface 20a. The gas blanket B stays in place above the top surface of the metallic material as a result of its higher density than air and can be supplied with additional gas over time as necessary to maintain the blanket.

[0012] The liquid cooling pool 20 comprises a thermally conductive liquid material, such as a molten metal or alloy, having a melting point lower than that of the amorphous metallic material M discharged thereon from nozzle opening 16. The liquid material comprising the liquid cooling pool 20 preferably does not react or alloy with the amorphous metallic material discharged and solidified thereon in a manner that adversely affects its amorphous properties and has a density such that the amorphous metallic material will float on the surface 20a of the pool 20. The temperature of the liquid cooling pool 20 is maintained below the temperature of the molten metallic material M discharged from the crucible 10. The liquid cooling pool 20 provides a high enough cooling rate to rapidly solidify the molten metallic material M within for example only, 10 seconds of its contacting the pool surface 20a.

[0013] For purposes of illustration and not limitation, a molten tin pool maintained at a temperature of 450 to 500 degrees F can be used to rapidly solidify a molten amorphous metallic material. For example, the molten tin pool can be used to rapidly solidify a conventional aluminum based amorphous alloy that is discharged from crucible 10 at a temperature of 1300 degrees F (alloy melting point of 1200-1250 degrees F) and at a rate of 1 to 10 pounds/second. A solidified amorphous sheet may be produced having an exemplary thickness of about 0.1 to about 0.3 inch, an exemplary width of about

4 to about 12 inches and exemplary length of about 12 to about 36 inches and a microstructure that is substantially 100% amorphous or glassy.

[0014] The vessel 22 includes a laterally elongated ceramic end stop 32 proximate the nozzle opening 16 and extending substantially parallel with the nozzle opening 16. The ceramic stop 32 defines an end of the sheet of molten metallic material M as it is discharged and spreads over onto the flat, quiescent upper surface 20a of the pool 20. In Figure 2, the width dimension W of pool 20 between side walls 22a of the vessel 22 defines the width dimension of the amorphous sheet S to be produced since the molten amorphous metallic material discharged from the nozzle opening 16 will spread out over pool surface 20a and encounter and be confined by the opposite lateral side walls 22a. The nozzle opening 16 optionally may have a width dimension that is generally equal to the width dimension between side walls 22a, rather than the nozzle size shown. In Figure 3, the width dimension of the amorphous sheet alternately can be defined between refractory side members 23 spaced from vessel walls 22a and immersed in the pool 20 at appropriate locations from the vessel walls 22a to define the desired width of the sheet to be produced. The side members 23 can be adjustably mounted on vessel walls 22a to this end.

[0015] The thickness of the amorphous sheet S to be produced is controlled by the rate at which the molten metallic material M is discharged from nozzle opening 16 onto pool surface 20a as controlled by the stopper rod 18 as well as the withdrawal rate of solidified amorphous sheet from the pool surface 20a on rollers 40, some or all of which rollers are driven to rotate by one or more conventional roller drive motors 55 (one shown schematically). In particular, the primary thickness control employs a laser level control sensor 50 that senses the height (thickness) of the metallic material M (either molten or solidified) on the pool surface 20a and provides feedback signals to stopper rod actuator 21, such as an electrically driven stopper rod actuator. The actuator 21 adjusts the position of stopper rod 18 relative to nozzle opening 16 to control the rate of supply of molten amorphous metallic material to pool 20 in response to the feedback signals representative of the height (thickness) of the molten metallic material M on pool surface 20a to maintain a uniform sheet thickness.

[0016] The solidified end E of the amorphous sheet S is withdrawn by the rollers 40 at a controlled rate to this end as well. The amorphous sheet S is withdrawn from pool surface 20a in a direction parallel to the pool surface 20a. The solidified end of sheet S is withdrawn through a seal 60 that minimizes leakage of the cooling liquid of pool 20.

[0017] The length of the amorphous sheet S is controlled by the total amount of molten metallic material M continuously supplied over time from the crucible 10 through the nozzle opening 16 onto the pool surface 20a and withdrawn as a solidified amorphous sheet S. The

solidified amorphous sheet can be produced to a selected length that may optionally be coiled.

[0018] Although the invention has been described in detail above with respect to certain embodiments, those skilled in the art will appreciate that modifications, changes and the like can be made therein without departing from the spirit and scope of the invention as set forth in the appended claims.

Claims

1. A method of making a sheet of amorphous metallic material, comprising discharging a molten metallic material onto a surface of a liquid cooling pool and solidifying the molten metallic material on said surface rapidly enough to form an amorphous sheet of said metallic material on said surface. 15
2. The method of claim 1 wherein said molten metallic material discharged on said surface assumes a width dimension of said pool. 20
3. The method of claim 2 wherein said molten metallic material discharged on said surface assumes a width dimension of a vessel in which said pool resides. 25
4. The method of claim 1 wherein said molten metallic material discharged on said surface assumes a width dimension of side members immersed in the pool. 30
5. The method of claim 1 wherein said molten metallic material is discharged on said surface of said pool which comprises a thermally conductive liquid material at a temperature lower than that of said molten metallic material. 35
6. The method of claim 5 wherein said thermally conductive liquid material comprises a molten metal or alloy having a lower melting point than that of the molten metallic material discharged thereon. 40
7. The method of claim 6 wherein said molten metal or alloy comprises molten tin. 45
8. The method of claim 1 including withdrawing the amorphous sheet from said surface in a direction parallel to said surface. 50
9. The method of claim 1 wherein the molten metallic material is fed onto the pool surface at a rate to control the thickness dimension of said amorphous sheet. 55
10. The method of claim 9 wherein the height of the metallic material on said surface is sensed.
11. The method of claim 10 wherein said molten metallic material is fed onto the pool surface from a crucible in response to the sensed height.
12. The method of claim 1 including providing an inert or non-reactive gas above said molten metallic material discharged onto said surface and above said amorphous sheet.

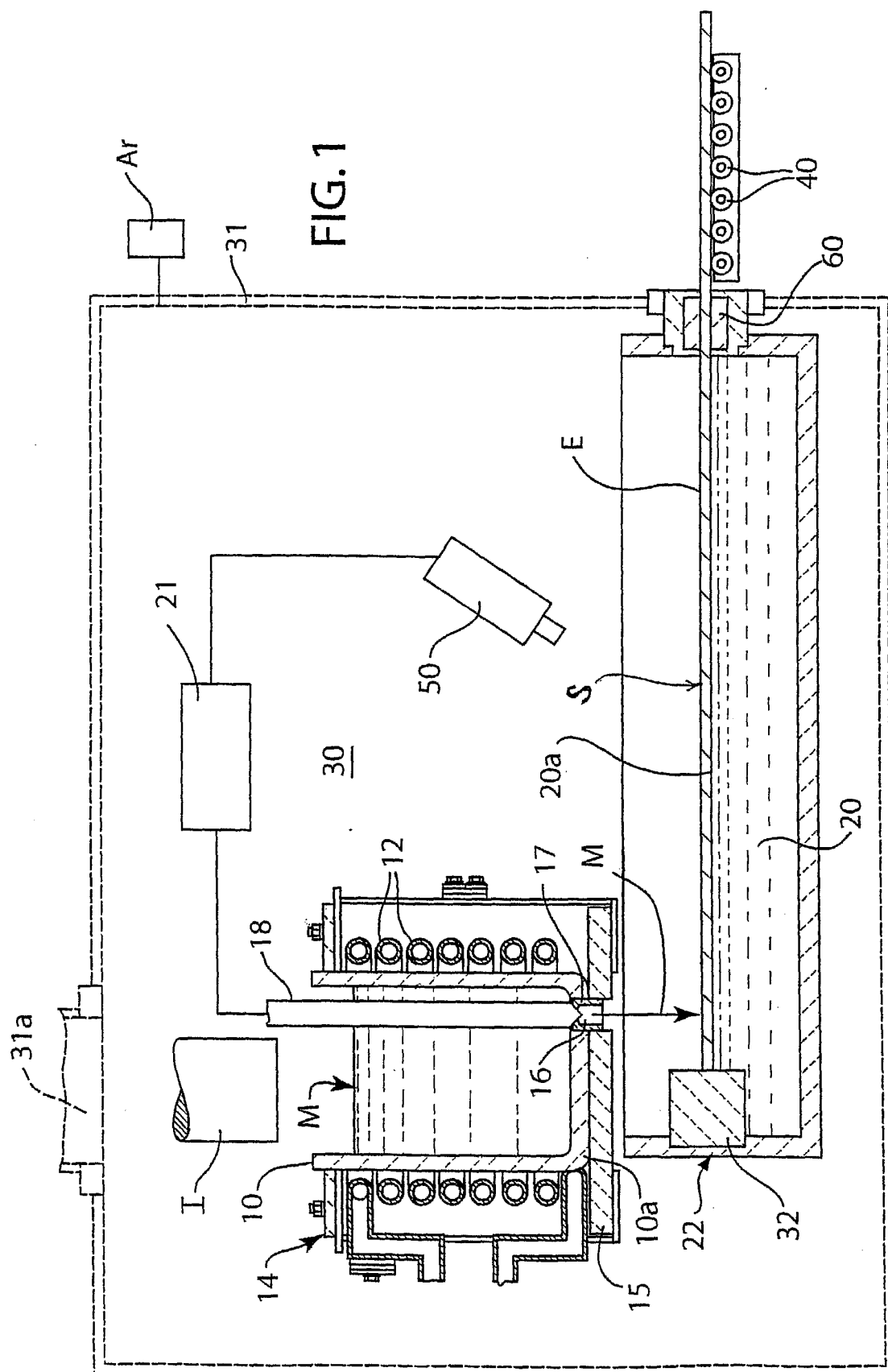


FIG. 2

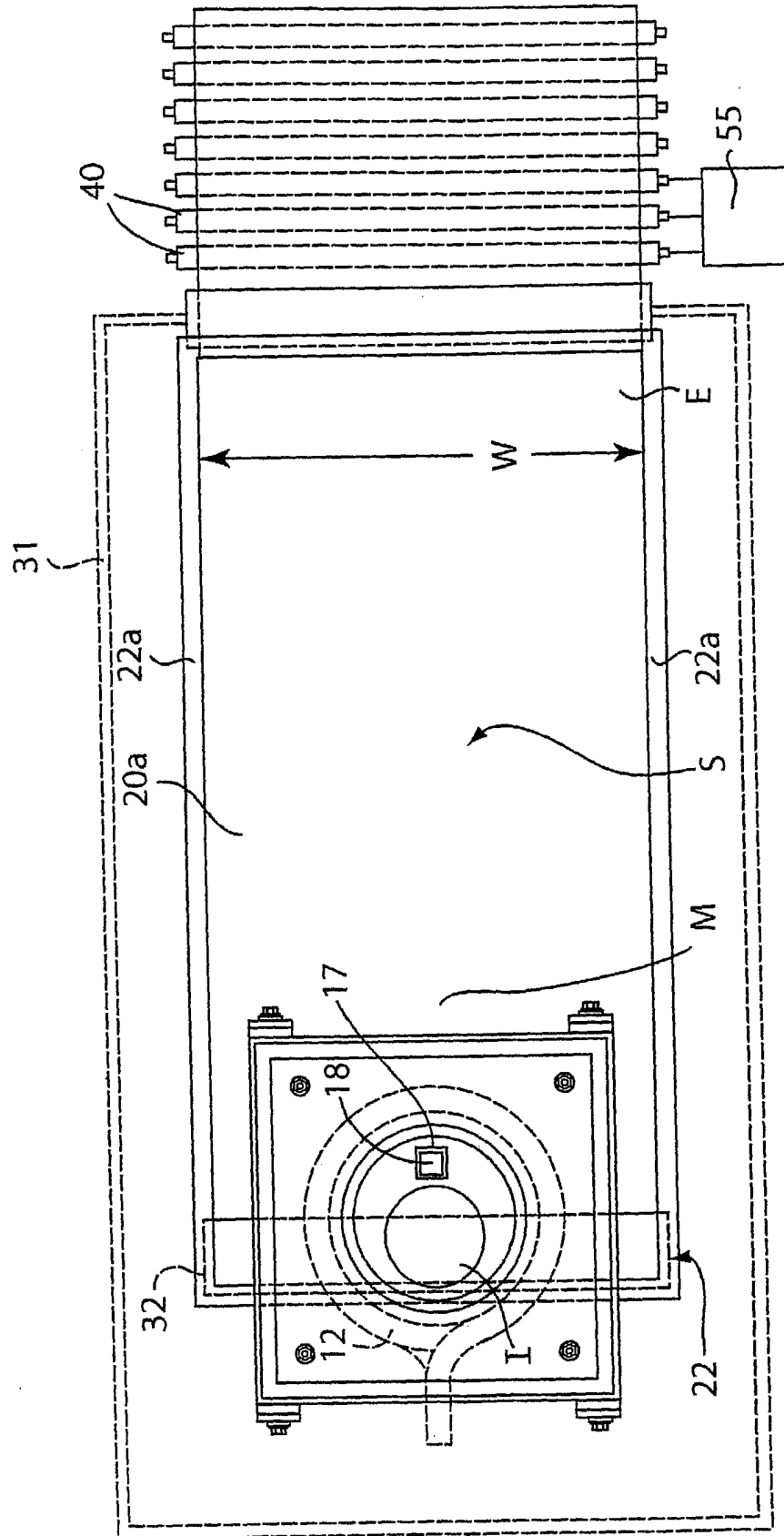


FIG. 3

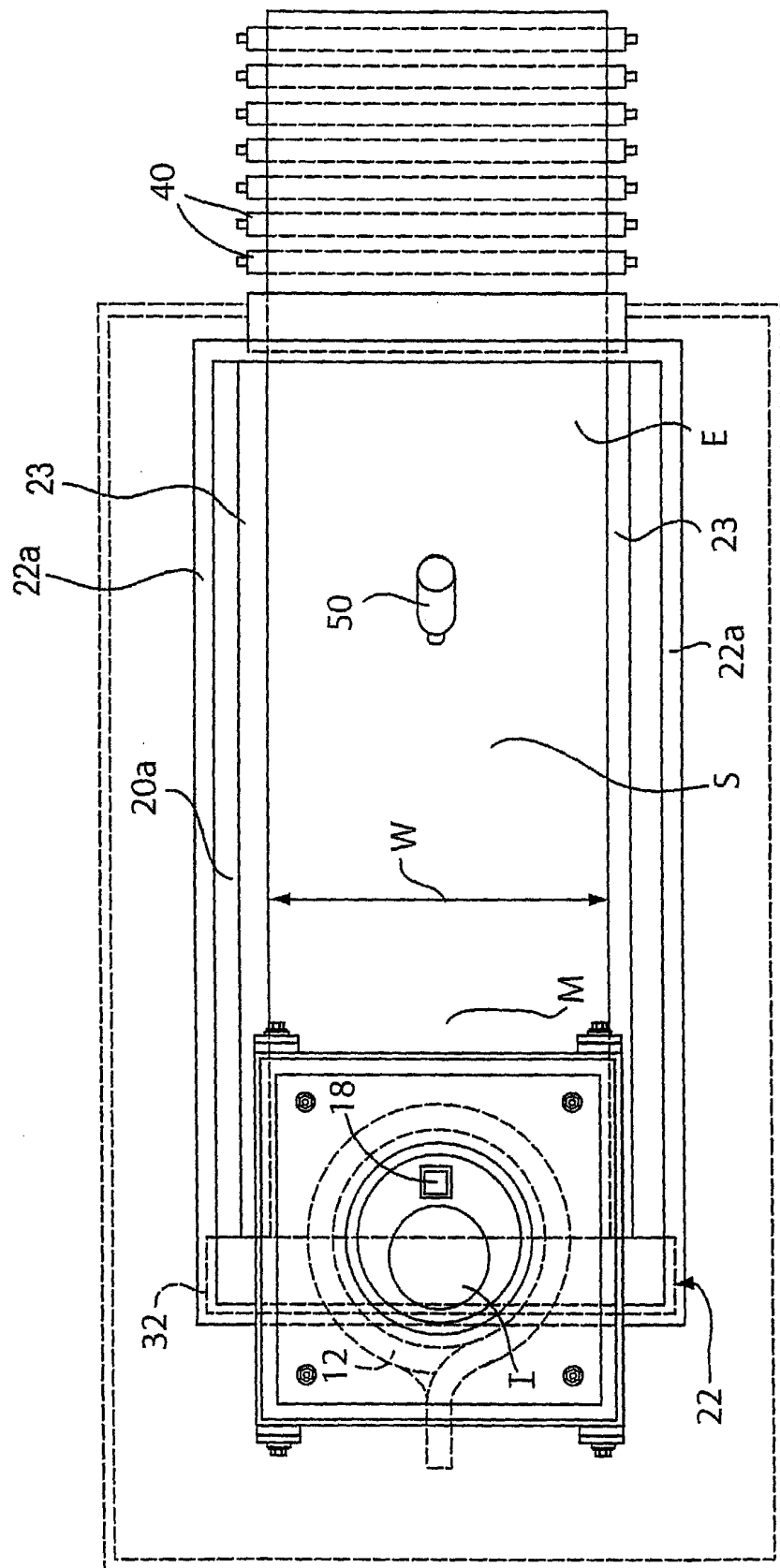
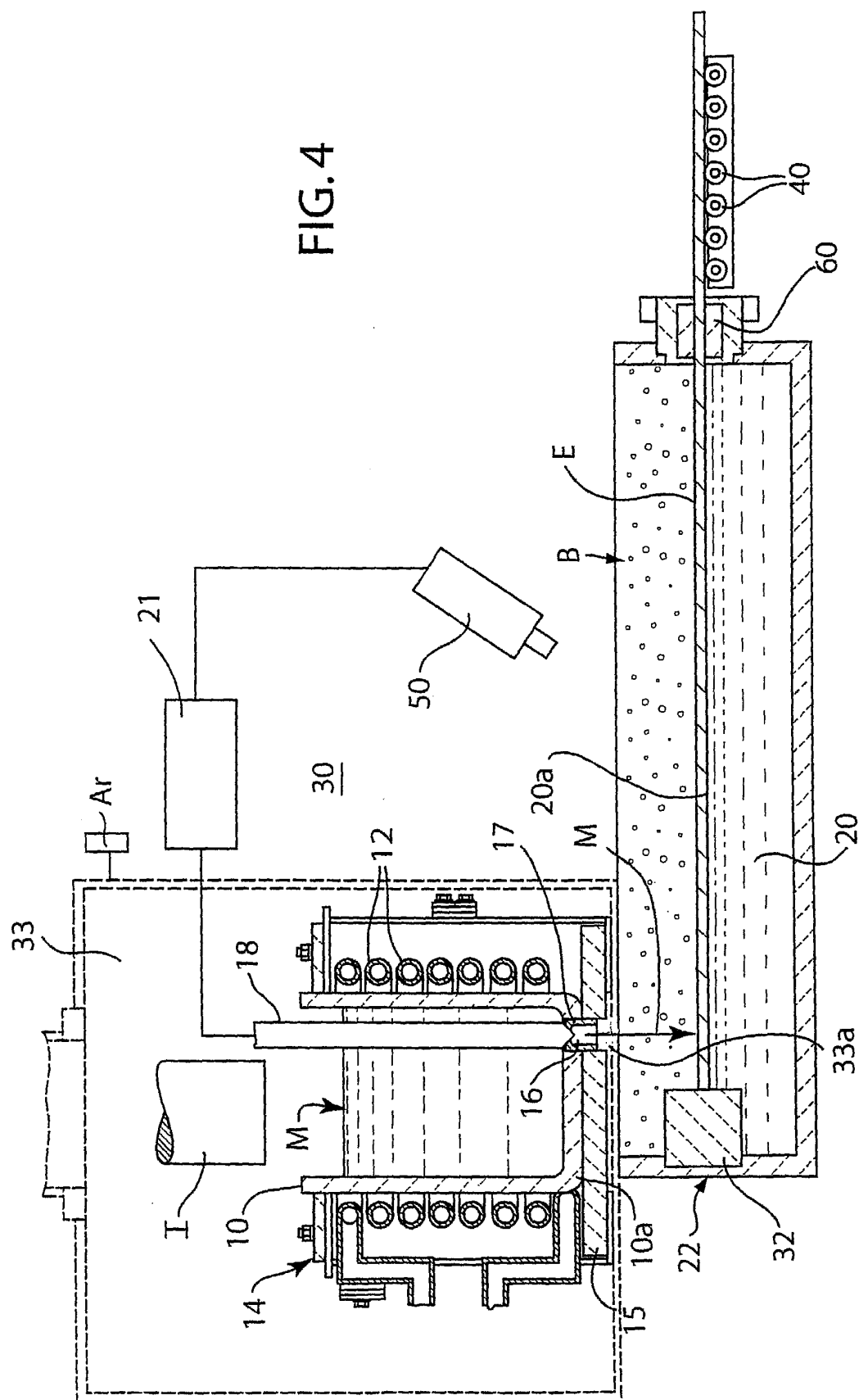


FIG. 4





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 00 6039

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	FR 2 652 019 A (SIDERURGIE FSE INST RECH) 22 March 1991 (1991-03-22) * page 2, line 18 - page 3, line 26; claims 1-3; figures 1,2 *	1-3,5,6, 8,12	B22D11/01
A	EP 0 679 459 A (MIURA TOSHIHIKO) 2 November 1995 (1995-11-02) * claims 1-4 *	1-6,8,12	
A	PATENT ABSTRACTS OF JAPAN vol. 007, no. 169 (M-231), 26 July 1983 (1983-07-26) & JP 58 074249 A (MITSUBISHI JUKOGYO KK), 4 May 1983 (1983-05-04) * abstract *	1,4-6,8	
A	FR 1 433 230 A (DAVY & UNITED ENG CO LTD) 25 March 1966 (1966-03-25) * page 1, left-hand column, line 37 - page 2, left-hand column, line 20; figure *	1-3,5,6, 8,12	
A	EP 0 099 599 A (AKZO NV) 1 February 1984 (1984-02-01) * claim 1 *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7) B22D
Place of search THE HAGUE		Date of completion of the search 22 July 2003	Examiner Mailliard, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P4/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 00 6039

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-07-2003

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
FR 2652019	A	22-03-1991	FR	2652019 A3	22-03-1991
EP 0679459	A	02-11-1995	EP	0679459 A1	02-11-1995
			WO	9411133 A1	26-05-1994
JP 58074249	A	04-05-1983	NONE		
FR 1433230	A	25-03-1966	NONE		
EP 0099599	A	01-02-1984	AT	18726 T	15-04-1986
			DE	3362675 D1	30-04-1986
			EP	0099599 A1	01-02-1984
			JP	1789794 C	29-09-1993
			JP	4078391 B	11-12-1992
			JP	59024556 A	08-02-1984

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82